A New General Approach t Bicyclopropylidenes†

Armin de Meijere,*,‡ Sergei I. Kozhushkov,‡,§ Thomas Spaeth,‡ and Nikolai S. Zefirov§

Institut für Organische Chemie, Georg-August-Universität Göttingen, D-3400 Göttingen, Germany, and Department of Chemistry, Moscow State University, 119899, Moscow, Russia

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Recently we have reported several synthetic approaches to branched triangulanes (oligospiroalkanes consisting only of three-membered rings).[1,2] Unfortunately, most of these are rather complicated multistep syntheses. The most convenient approach is based on a methodology previously used in the synthesis of unbranched triangulanes,[3,4] i.e. cycloaddition of (chloromethyl)carbene to an appropriate bicyclopropylidene,[5] dehydrochlorination with potassium *tert*-butoxide in DMSO,[1-5] and finally cyclopropanation with diazomethane under palladium(II) acetate catalysis.[1-6] However, the inaccessibility of higher oligospirocyclopropane-annealated bicyclopropylidenes is an essential limitation of this approach. We have therefore developed a new methodology, which is widely applicable to unsubstituted bicyclopropylidene[7-9] as well as spirocyclopropanated bicyclopropylidenes.

Results and Discussion

As recently reported[10] a number of methyl carboxylates react with ethylmagnesium bromide in the presence of tetraisopropoxytitanium to form 1-substituted 1-cyclopropanols. We have now found that this reaction is also applicable to methyl cyclopropanecarboxylate (**1**) and gives 1-cyclopropyl-1-cyclopropanol (**2**) in almost quantitative yield. Adopting our previous experience,[8,9] it is now possible to prepare bicyclopropylidene (**4**) in synthetically useful quantities of 40–45 g within 1 week (Scheme I).[11]

This sequence can be made repetitive, as the rhodium acetate catalyzed addition of diazoacetic ester[12] to methylenecyclopropanes[1,4] and bicyclopropylidenes[7-9,13-15] may yield spirocyclopropanated cyclopropanecarboxylates which in turn can be converted to oligospiropropanated bicyclopropylidenes. Thus bicyclopropylidene (**4**) gave carboxylate **5**, which was converted to cyclopropanol **6** (99% yield) and further to **7** (75%) and dispirocyclopropanated bicyclopropylidene **8** (66%) (Scheme II). This is a more convenient route to **8** than earlier ones, which either gave a difficultly separable mixture with bromobenzene[13] or low yields.[14]

Analogously, spiropentanecarboxylate (**9**), prepared from methylenecyclopropane (**13**), was converted to cyclopropylidenespiropentane (**12**) in three steps (overall yield 53%) (Scheme III). This approach has allowed compound **12** to be obtained on a preparative scale for the first time (cf. ref 15). Dispiro[2.0.2.1]heptanecarboxylates (**15**) are obtained as a mixture of exo (**15a**) and endo isomers (**15b**) (3:2).[16] This mixture was converted to a mixture of cyclopropanols **17a,b** (94% yield), which could be separated by column chromatography. Separate bromination of **17a** and **17b** gave the corresponding two isomeric bromides **16a,b** (75 and 73% yield) which were both dehydrobrominated to the same previously unknown bicyclopropylidene **18** (64%).

This same sequence is also applicable to diesters, e.g. as formed by 2-fold cyclopropanation of dicyclopropylidenemethane[15,17,18] (**19**) with ethyl diazoacetate (Scheme IV). Only two out of three possible diastereomers, namely **21a** and **21b**, were separated from the reaction mixture by column chromatography in a ratio of 1:1.2 and identified on the basis of their ^1H and ^{13}C NMR spectra, taking the different symmetries of the two molecules into consideration: the main (*Z,E*)-isomer **21b** has no elements of symmetry, the other two possible isomers have a C_2 axis, and the atoms C^8 and C^9 and groups attached to them form equivalent pairs. The second obtained isomer has the (*E,E*)-configuration as in **21a** (the formation of the sterically much more congested (*Z,Z*)-diester ought to be disfavored). Corresponding spectroscopic evidences were collected for the diols **23a,b** and dibromides **22a,b**, obtained from **21a** and **21b**. The bromination of diol **23b** to **22b** was accompanied by partial ring opening with the

* Author to whom correspondence should be addressed.
† Dedicated to Professor Klaus Hafner on the occasion of his 65th birthday.
‡ Georg-August-Universität Göttingen.
§ Moscow State University.

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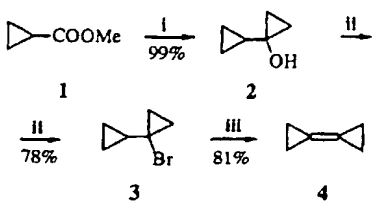
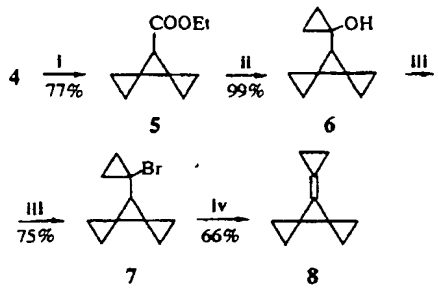
Scheme I[a]



[a] (i) EtMgBr, Ti(*i*-PrO)$_4$ (22 mol %), Et_2O, 20 °C, 3 h; (ii) $Ph_3P{\cdot}Br_2$, Py, CH_2Cl_2, 20 °C, 24 h; (iii) *t*-BuOK, DMSO, 20 °C, 24 h.

Scheme II[a]



[a] (i) $N_2CHCOOEt$, $[Rh(OAc)_2]_2$ (1 mol %), CH_2Cl_2, 0 °C, 12 h; (ii) EtMgBr, Ti(*i*-PrO)$_4$ (22 mol %), Et_2O, 20 °C, 3 h; (iii) $Ph_3P{\cdot}Br_2$, Py, CH_2Cl_2, 20 °C, 24 h; (iv) *t*-BuOK, DMSO, 20 °C, 5 h.

formation of dibromide **25**, as assigned on the basis of the NMR spectra. Dehydrobromination of both dibromides **22a,b** leads to the same diene **24**, which is sufficiently stable to be isolated, but partially decomposes during formation and purification by column chromatography.

This methodology has its limitations, though. While the reaction of *tert*-butyl 2-*n*-butoxycyclopropane-1-carboxylate (**26**) with ethylmagnesium bromide in the presence of Ti(*i*-PrO)$_4$ went remarkably well to give 1-(2′-*n*-butoxy-1′-cyclopropyl)-1-cyclopropanol (**27**) in sufficiently good yield (52%) (Scheme V), the attempted bromination of **27** with $Ph_3P{\cdot}Br_2$ in dichloromethane lead to complete decomposition of the starting material rather than the 2′-*n*-butoxy-substituted 1-bromobicyclopropyl **28**. Thus, functionally substituted bicyclopropylidenes can probably not be made along this route.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$. All solvents and reagents were purified and dried by standard techniques. Ether and pentane extracts were dried over $MgSO_4$. Methylenespiropentane (**14**),[4] *tert*-butyl (*E*)-2-(*n*-butyloxy)-cyclopropane-1-carboxylate (**26**),[20] and dicyclopropylidenemethane (**19**)[15,17,18] were prepared according to literature procedures.

General Procedure for Cycloaddition of (Ethoxycarbonyl)carbene to Olefins 4, 13, and 14 and Allene 19. Preparation of Esters 5, 9, and 15a,b and Diesters 21a,b. To a solution of an olefin (50 or 70 mmol for **13**) and dirhodium tetraacetate (0.5 mmol) in dichloromethane (20 mL) was added ethyl diazoacetate (55 mmol for **4**, **13**, and **14** and 125 mmol for **19**) over 12 h at 0 °C. The reaction mixture was then filtered through silica gel. After evaporation of the solvent, esters **5**, **9**, and **15a,b** were isolated by distillation, diesters **21a,b** by column chromatography over silica gel.

Ethyl Dispiro[2.0.2.1]heptane-7-carboxylate (5). Alkene **4** (5.30 g, 66.2 mmol) was converted to 8.47 g (77%) of **5** as described above: bp 84–85 °C (17 mbar); ^1H NMR δ 0.65–0.85 (m, 4 H), 0.85–1.05 (m, 4 H), 1.22 (t, 3 H, J = 7.2 Hz), 2.20 (s, 1 H), 4.08 (q, 2 H, J = 7.2 Hz); ^{13}C NMR δ 5.00, 6.21 (2 CH_2), 14.39 (CH_3), 22.65 (2 C), 26.44 (CH), 59.94 (CH_2), 173.13 (C). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.13; H, 8.57.

Ethyl Dispiro[2.0.2.1]heptane-1-carboxylate (15a,b).[16] Alkene **14** (10.15 g, 0.127 mol) was converted to 14.99 g (71%) of a 3:2 mixture of exo (**15a**) and endo isomer (**15b**): bp 82–85 °C (16 mbar).

Ethyl Spiropentanecarboxylate (9). Alkene **13** (7.57 g, 8.9 mL, 0.14 mol) was treated with ethyl diazoacetate (11.41 g, 0.1 mol) as described above to give **9** (12.01 g, 86%): bp 74–76 °C (28 mbar);[21] ^1H NMR δ 0.62–0.82 (m AA′BB′, 4 H), 1.06 (t, 3 H, J = 7.1 Hz), 1.14–1.20 (dd, 1 H, J = 3.5 and 7.4 Hz), 1.31 (t, 1 H, J = 4.0 Hz), 1.74–1.80 (dd, 1 H, J = 4.2 and 7.4 Hz), 3.89–4.01 (qd, 2 H, J = 3.8 and 7.1 Hz); ^{13}C NMR δ 4.89, 6.35, 14.61, 59.61 (CH_2), 14.04 (CH_3), 20.16 (CH), 18.18, 173.36 (C).

Ethyl (*E,E*)- and (*E,Z*)-Trispiro[2.0.0.2.1.1]nonane-8,9-dicarboxylate (21a,b). Allene **19** (1.775 g, 19.26 mmol) was treated as described above. After column chromatography over 350 g of silica gel (4 × 50-cm column, 1:3 ether/pentane) ethyl 2-cyclopropylidenespiropentane-1-carboxylate (**20**)[18] (23%), **21a** (1.217 g, 24%), and **21b** (1.461 g, 29%) were obtained. **21a**: R_f = 0.33; mp ~25 °C; ^1H NMR δ 0.8–0.95 (m, 4 H), 0.95–1.05 (m, 4 H), 1.17 (t, 6 H, J = 7.1 Hz), 2.38 (s, 2 H), 4.03 (q, 4 H, J = 7.1 Hz); ^{13}C NMR δ 3.87, 4.79, 60.13 (2 CH_2), 14.20 (2 CH_3), 28.07 (2 CH), 21.84, 171.99 (2 C), 31.25 (C). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.04; H, 7.66. **21b**: R_f = 0.39; mp 43–45 °C; ^1H NMR δ 0.65–0.98 (m, 6 H), 0.98–1.12 (m, 2 H), 1.16 (t, 3 H, J = 7.2 Hz), 1.19 (t, 3 H, J = 7.2 Hz), 2.07 (s, 1 H), 2.37 (s, 1 H), 4.03 (q, 2 H, J = 7.2 Hz), 4.17 (q, 2 H, J = 7.2 Hz); ^{13}C NMR δ 3.38, 4.25, 5.20, 6.12, 60.01, 60.19 (CH_2), 14.18, 14.25 (CH_3), 25.10, 26.02 (CH), 22.11, 22.17, 32.16, 171.86, 171.93 (C). Anal. Found: C, 68.04; H, 7.66.

General Procedure for the Preparation of Cyclopropanols 2, 6, 10, 17a,b, 23a,b, and 27 from Esters 1, 5, 9, 15a,b, 21a,b, and 26. To a well-stirred solution of ester (45 mmol) or diester (22.5 mmol) and Ti(*i*-PrO)$_4$ (3 mL) in dry ether (120 mL) an ethereal solution of EtMgBr (93 mmol) was added dropwise over 3 h at 20 °C. The mixture was cooled to 0 °C and carefully quenched with 50 mL of 10% aqueous H_2SO_4. The organic layer was washed with a saturated $NaHCO_3$ solution and saturated brine, dried, and concentrated in vacuo (water pump) at 10 °C. The product was purified by column chromatography on silica gel (alcohols **17a,b**, **23a,b**, and **27**) or brominated without further purification (alcohols **2**, **6**, and **10**).

1-Cyclopropyl-1-cyclopropanol (2).[8] was obtained in 99% yield (97.16 g) from the commercially available methyl cyclopropanecarboxylate (**1**) (100.12 g, 1 mol).

1-(7′-Dispiro[2.0.2.1]heptyl)-1-cyclopropanol (6). Ester **5** (26.394 g, 0.159 mol) was converted to 23.645 g (99%) of **6** as described above: mp 44–45 °C; ^1H NMR δ 0.4–0.46 (m, 2 H), 0.48–0.55 (m, 4 H), 0.55–0.64 (m, 2 H), 0.75–0.82 (m, 4 H), 1.92 (s, 1 H), 2.74 (s, OH); ^{13}C NMR δ 3.46, 4.88, 11.58 (2 CH_2), 27.18 (CH), 17.35 (2 C), 56.35 (C). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.71; H, 9.41.

1-Spiropentyl-1-cyclopropanol (10). Ester **9** (11.93 g, 85.1 mmol) was converted to 10.57 g (97%) of **10** as described above: oil; ^1H NMR δ 0.23–0.31 (m, 1 H), 0.43–0.74 (m, 8 H), 0.86–0.91 (dd, 1 H, J = 4.0 and 7.7 Hz), 1.59–1.64 (dd, 1 H, J = 4.5 and 7.7 Hz), 2.90 (s, OH); ^{13}C NMR δ 3.72, 5.43, 10.64, 11.08, 12.12 (CH_2), 22.55 (CH), 12.41, 56.77 (C). Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found C, 77.24; H, 9.76.

1-(1′-Dispiro[2.0.2.1]heptyl)-1-cyclopropanol (17). A mixture of esters **15a,b** (4.99 g, 30 mmol) was treated as described above. After column chromatography over 400 g of silica gel (5 × 50-cm column, 3:2 pentane/ether) exo (**17a**) (2.542 g, 56%) and endo isomers (**17b**) (1.694 g, 38%) were obtained (total yield 94%). **17a**: R_f = 0.35; mp 71–73 °C; ^1H NMR δ 0.33–0.42 (m, 1 H), 0.48–0.63 (m, 4 H), 0.68–0.82 (m, 5 H), 1.06 (d, 1 H, J = 4.2 Hz), 1.14 (d, 1 H, J = 4.2 Hz), 1.39–1.44 (dd, 1 H, J = 5.2 and 8.3 Hz), 2.63 (s, OH); ^{13}C NMR δ 5.24, 5.36, 10.0, 10.83, 11.02, 12.29 (CH_2), 21.77 (CH), 13.30, 18.07, 56.93 (C). Anal. Calcd for

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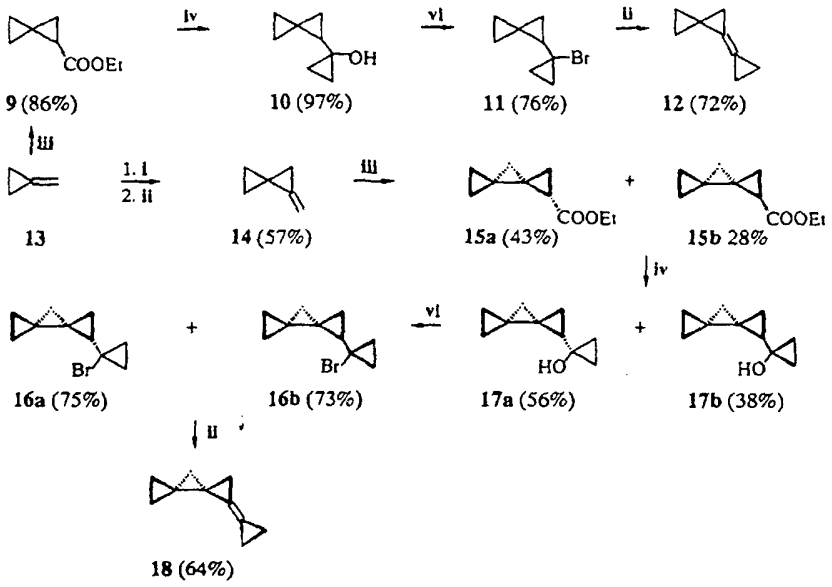
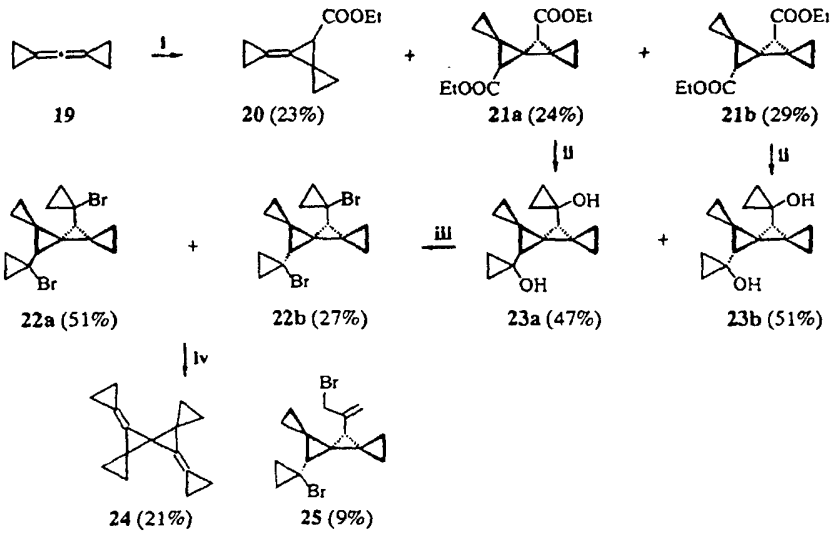
Scheme III[a]



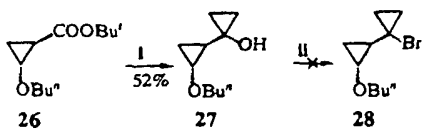
[a] (i) CH_3CHCl_2, $NaN(SiMe_3)_2$, 0 °C, 48 h; (ii) *t*-BuOK, DMSO, 70 °C, 1 h for **14** or 20 °C, 5 h for **18**; (iii) $N_2CHCOOEt$, $[Rh(OAc)_2]_2$ (1 mol %), CH_2Cl_2, 0 °C, 12 h; (iv) EtMgBr, $Ti(i\text{-}PrO)_4$ (22 mol %), Et_2O, 20 °C, 3 h; (vi) $Ph_3P{\cdot}Br_2$, Py, CH_2Cl_2, 20 °C, 24 h.

Scheme IV[a]



[a] (i) $N_2CHCOOEt$, $[Rh(OAc)_2]_2$ (1 mol %), CH_2Cl_2, 0 °C, 12 h; (ii) EtMgBr, $Ti(i\text{-}PrO)_4$ (22 mol %), 20 °C, 3 h; (iii) $Ph_3P{\cdot}Br_2$, Py, CH_2Cl_2, 20 °C, 24 h; (iv) *t*-BuOK, DMSO, 20 °C, 5 h.

Scheme V[a]



[a] (i) EtMgBr, $Ti(i\text{-}PrO)_4$ (22 mol %), Et_2O, 20 °C, 3 h; (ii) $Ph_3P{\cdot}Br_2$, Py, CH_2Cl_2, 20 °C, 5 h.

$C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.97; H, 9.41. **17b**: R_f = 0.39; mp 25 °C; ^1H NMR δ 0.07–0.18 (m, 1 H), 0.18–0.27 (m, 1 H), 0.27–0.33 (m, 1 H), 0.41–0.52 (m, 1 H), 0.52–0.68 (m, 2 H), 0.68–0.77 (m, 1 H), 0.77–0.87 (m, 2 H), 0.87–0.98 (m, 1 H), 1.05 (d, 1 H, J = 4.1 Hz), 1.13 (d, 1 H, J = 4.1 Hz), 1.81–1.89 (dd, 1 H, J = 4.9 and 8.3 Hz), 2.33 (s, OH); ^{13}C NMR δ 5.11, 5.82, 9.81, 11.14, 11.70, 13.15 (CH_2), 12.80, 18.33, 56.39 (C), 23.94 (CH). Anal. Found: C, 79.79; H, 9.40.

(*E*,*E*)- (23a) and (*Z*,*E*)-8,9-Bis(1'-hydroxycyclopropyl)-trispiro[2.0.0.2.1.1]nonane (23b). **23a** (0.454 g, 47%) was obtained as described above from **21a** (1.10 g, 4.16 mmol) after column chromatography over 50 g of silica gel (2- × 30-cm column, ether): R_f = 0.33; mp 71–73 °C; ^1H NMR δ 0.17–0.28 (m, 2 H), 0.31–0.38 (m 2 H), 0.38–0.51 (m, 2 H), 0.54–0.64 (m, 2 H), 0.64–0.77 (m, 4 H), 0.77–0.87 (m, 4 H), 2.0 (s, 2 OH), 2.18 (s, 2 H); ^{13}C NMR δ 1.63, 4.52, 11.13, 12.45 (2 CH_2), 27.98 (2 CH), 15.55, 55.98 (2 C), 25.0 (C). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C. 77.51; H, 8.70. **23b** (0.583 g, 51%) was obtained as described above from **21b** (1.30 g, 4.92 mmol) after column

chromatography under the same conditions: oil; R_f = 0.42; ^{1}H NMR δ 0.16–0.62 (m, 8 H), 0.62–0.81 (m, 6 H), 0.83–1.0 (m, 2 H), 1.37 (s, 1 H), 2.18 (s, 1 H), 3.07 (s, 2 OH); ^{13}C NMR δ 1.94, 3.08, 3.63, 4.49, 10.62, 12.06, 12.18, 12.29 (CH_2), 26.37, 27.18 (CH), 15.45, 16.64, 24.12, 55.0, 56.07 (C). Anal. Found: C, 77.47; H, 8.67.

(*E*)-1-(2′-(Butyloxy)-1′-cyclopropyl)-1-cyclopropanol (27). Ester **26** (1.134 g, 5.24 mmol) was converted to 0.464 g (52%) of **27** (after column chromatography over 40 g of silica gel, 1.5- × 40-cm column, 3:2 pentane/ether): oil; R_f = 0.28; ^{1}H NMR δ 0.27–0.33 (m, 2 H), 0.33–0.43 (m, 1 H), 0.58–0.66 (m, 2 H), 0.66–0.77 (m, 1 H), 0.84 (t, 3 H, J = 7.2 Hz), 1.10–1.55 (m, 5 H), 2.99–3.08 (m, 1 H), 3.21 (s, OH), 3.38 (t, 2 H, J = 6.5 Hz); ^{13}C NMR δ 10.86, 11.73, 11.96, 19.23, 31.51, 70.41 (CH_2), 13.75 (CH_3), 24.54, 57.18, (CH), 54.25 (C). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.44; H, 10.60.

General Procedure for the Bromination of Alcohols 2, 6, 10, and 17a,b and Diols 23a,b. Preparation of Bromides 3, 7, 11, and 16a,b and Dibromides 22a,b. To a cooled (−15 °C), well-stirred solution of triphenylphosphine (2.75 g, 10.5 mmol) in dry dichloromethane (40 mL) was added bromine (0.54 mL, 10.5 mmol) in dry CH_2Cl_2 (2 mL) dropwise over 10 min. After additional stirring for 15 min, a solution of alcohol (10 mmol) or diol (5 mmol) and pyridine (0.86 mL, 10.5 mmol) in dry dichloromethane (5 mL) was added dropwise at −30 °C. The mixture was stirred for 4 h at −10 °C and 24 h at rt. After evaporation of the solvent, the residue was thoroughly washed with pentane and filtered. The filtrate, after evaporation of the solvent, was distilled "bulb-to-bulb" in vacuo (0.01 Torr) (for the bromides **7**, **11**, **16a,b**) or dehydrobrominated without further purification (dibromides **22a,b**). Bromide **3**: The reaction mixture was distilled "bulb-to-bulb" in vacuo (0.01 Torr) into a cooled trap (−196 °C); the residue was thoroughly washed with pentane and filtered. The combined solutions were carefully concentrated and distilled under reduced pressure.

(1′-Bromocyclopropyl)cyclopropane (3). Alcohol **2** (97.16 g, 0.99 mol) was converted to 118.0–124.36 g (74–78%) of **3** as described above: bp 69–71 °C (120 mbar).[9]

7-(1′-Bromocyclopropyl)dispiro[2.0.2.1]heptane (7). Alcohol **6** (23.5 g, 0.156 mol) was converted to 24.93 g (75%) of **7** as described above: ^{1}H NMR δ 0.50–0.65 (m, 4 H), 0.75–0.85 (m, 2 H), 0.85–0.95 (m, 4 H), 0.95–1.05 (m, 2 H), 2.29 (s, 1 H); ^{13}C NMR δ 3.20, 5.01, 14.14 (2 CH_2), 22.95 (CH), 19.79 (2 C), 36.22 (C).

(1-Bromocyclopropyl)spiropentane (11). Alcohol **10** (10.4 g, 83.75 mmol) was converted to 11.91 g (76%) of **11** as described above: ^{1}H NMR δ 0.52–0.8 (m, 4 H), 0.82–1.07 (m, 5 H), 1.14–1.28 (m, 1 H), 1.94–1.99 (dd, 1 H, J = 4.5 and 7.7 Hz); ^{13}C NMR δ 3.44, 5.50, 12.85, 14.09, 14.18 (CH_2), 26.02 (CH), 15.69, 36.42 (C).

***exo*-1-(1′-Bromocyclopropyl)dispiro[2.0.2.1]heptane (16a).** Alcohol **17a** (2.30 g, 15.3 mmol) was converted to 2.45 g (75%) of **16a** as described above: ^{1}H NMR δ 0.4–1.38 (m, 12 H), 1.78–1.83 (dd, 1 H, J = 4.6 and 7.9 Hz); ^{13}C NMR δ 5.30, 5.38, 10.66, 12.43, 13.65, 14.66 (CH_2), 25.28 (CH), 13.91, 21.39, 36.54 (C). ***endo*-1-(1′-Bromocyclopropyl)dispiro[2.0.2.1]heptane (16b)** (1.554 g, 73%) was obtained from **17b** (1.50 g, 10 mmol) as described above: ^{1}H NMR δ 0.39–1.39 (12 H), 2.10–2.15 (dd, 1 H, J = 4.3 and 7.7 Hz); ^{13}C NMR δ 5.02, 6.35, 11.64, 13.33, 13.59, 14.94 (CH_2), 28.06 (CH), 12.73, 20.09, 36.38 (C).

(*E,E*)-8,9-Bis(1′-bromocyclopropyl)trispiro[2.0.0.2.1.1]nonane (22a). Diol **23a** (0.40 g, 1.72 mmol) was converted to 0.314 g (51%) of **22a** as described above: ^{1}H NMR δ 0.25–1.25 (m, 16 H), 2.29 (s, 2 H); ^{13}C NMR δ 1.01, 4.53, 12.84, 14.88 (2 CH_2), 30.71 (2 CH), 17.02, 33.59 (2 C), 28.44 (C). **(*E,Z*)-8,9-Bis(1′-bromocyclopropyl)trispiro[2.0.0.2.1.1]nonane (22b).** Diol **23b** (0.50 g, 2.15 mmol) was treated as mentioned above. After column chromatography over 40 g of silica gel (2- × 35-cm column, pentane) **22b** (0.208 g, 27%) and **8-(1-bromocyclopropyl)-9-(3-bromopropen-2-yl)trispiro[2.0.0.2.1.1]nonane (25)** (69 mg, 9%) were obtained. **22b**: ^{1}H NMR δ 0.45–1.40 (m, 16 H), 2.02, (s, 1 H), 2.55 (s, 1 H); ^{13}C NMR δ 2.39, 3.25, 3.41, 4.46, 13.95, 14.24, 14.39, 15.29 (CH_2), 29.48, 29.58 (CH), 18.73, 18.90, 28.49, 34.12, 35.73 (C). **25**: ^{1}H NMR δ 0.45–1.20 (m, 12 H), 2.06 (s, 1 H), 2.35 (s, 1 H), 3.8–3.92 (m AB, 2 H, J = 4.9 Hz), 4.61 (narrow m, 1 H), 5.10 (narrow m, 1 H); ^{13}C NMR δ 0.80, 3.43, 3.62, 6.34, 14.24, 14.37, 36.27, 113.66 (CH_2), 25.19, 29.03 (CH), 19.56, 21.33, 26.74, 35.75, 114.01 (C).

General Procedure for Dehydrobromination of Bromides 3, 7, 11, and 16a,b and Dibromides 22a,b. To potassium *tert*-butoxide (6.7 g, 60 mmol) in dry DMSO (40 mL) was added bromide (40 mmol) or a mixture of **23a,b** (20 mmol) in DMSO (5 mL) dropwise at 20 °C. The reaction mixture was stirred for 5 h at 20 °C (15 h for bromide **3**) and then quenched with cold water (60 mL). Pentane (80 mL) was added, and the organic layer was separated, washed with water, and dried. The pentane solution was carefully concentrated and distilled in vacuo. Diolefin **25** was separated by column chromatography.

Bicyclopropylidene (4) and Cyclopropylidenespiropentane (12). The reaction mixture was trap to trap distilled at 20 °C (0.01 Torr), and the product was collected in a cooled trap (−196 °C), washed thoroughly with water, and dried. The purity of bicyclopropylidene (**4**)[8,9] thus obtained is 95–97%; yield 44.33 g (81%) from 110 g (0.683 mol) of **3**. Compound **12** was distilled under reduced pressure.

7-Cyclopropylidenedispiro[2.0.2.1]heptane (8). Bromide **7** (24.0 g, 0.113 mol) was converted to 9.86 g (66%) of **8** as described above: bp 72.73 °C (30 mbar).[13,14]

Cyclopropylidenespiropentane (12).[15] From 11.0 g (58.8 mmol) of **11** was obtained alkene **12** (4.49 g, 72%) as described above: bp 77–79 °C (116 mbar); ^{1}H NMR δ 1.10–1.12 (m, 2 H), 1.13–1.26 (m, 6 H), 1.48–1.51 (p, 2 H, J = 1.8 Hz); ^{13}C NMR δ 9.15 (2 CH_2), 2.31, 2.89, 10.35 (CH_2), 11.52, 106.51, 116.24 (C).

1-Cyclopropylidenedispiro[2.0.2.1]heptane (18). A mixture of bromides **16a,b** (4.0 g, 18.77 mmol) was converted to 1.59 g (64%) of alkene **18** as described above: bp 71–73 °C (30 mbar); ^{1}H NMR δ 0.68–0.84 (m, 2 H), 0.85–0.97 (m, 2 H), 1.11–1.26 (m, 4 H), 1.35 (d, 1 H, J = 5.8 Hz), 1.53 (d, 1 H, J = 3.6 Hz), 1.55 (d, 1 H, J = 5.8 Hz), 1.58 (d, 1 H, J = 3.6 Hz); ^{13}C NMR δ 2.50, 3.13, 5.42, 6.20, 9.69, 16.14 (CH_2), 17.47, 17.60, 107.26, 115.44 (C). The structures of olefins **8**, **12**, and **18** were confirmed by low-temperature X-ray crystal structure analysis (Dr. R. Boese, Institute of Inorganic Chemistry, University of Essen); these results will be published separately.

8,9-Bis(cyclopropylidene)trispiro[2.0.0.2.1.1]nonane (24). A mixture of dibromides **22a,b** was treated as mentioned above. After column chromatography, over 10 g of silica gel (0.5- × 15-cm column, pentane) **24** (63 mg, 21%) was obtained: oil; R_f = 0.33; ^{1}H NMR δ 0.84–0.96 (m, 2 H), 1.03–1.15 (m, 4 H), 1.15–1.28 (m, 10 H); ^{13}C NMR δ 2.76, 2.96, 7.08, 8.54 (2 CH_2), 18.52, 105.39, 120.04 (2 C), 29.78 (C). Anal. Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.83; H, 8.17.

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Supplementary Material Available: ^{13}C and ^{1}H NMR spectra of **7**, **11**, **16a**, **22a**, **22b**, and **25** (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.